

Fluctuations and correlations in nonequilibrium systems

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Abstract. Nonequilibrium systems exchange the energy with an environment in the form of work and heat. The work done on a system obeys the fluctuation theorem, while the dissipated heat which differs from the work by the internal energy change does not. We derive the modified fluctuation relation for the heat in the overdamped Langevin system. It shows that mutual correlations among the work, the heat, and the internal energy change are responsible for the different fluctuation property of the work and the heat. The mutual correlation is investigated in detail in a two-dimensional linear diffusion system. We develop an analytic method which allows one to calculate the large deviation function for the joint probability distributions. We find that the heat and the internal energy change have a negative correlation, which explains the reason for the breakdown of the fluctuation theorem for the heat.

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1. Introduction

Consider a nonequilibrium stochastic system in thermal contact with a heat bath. It is driven out of equilibrium by a time-dependent perturbation or a nonconservative force. Due to absence of the detailed balance, a nonequilibrium system is characterized by a nonzero probability current and a net energy flow. Recently, nonequilibrium fluctuations of thermodynamic quantities such as a work, an entropy production, and a heat have been attracting growing interests. Various types of fluctuation theorems governing the nonequilibrium fluctuations have been found in a thermostated shearing fluid [1, 2], systems driven by a nonequilibrium work [3, 4], stochastic Langevin systems [5], master equation systems [6], systems in a nonequilibrium steady state [7], general stochastic systems [8, 9], feedback control systems [10], systems with odd parity variables [11, 12], and so on. Theoretically, the fluctuation theorems allow us to study the time irreversibility of nonequilibrium systems. At the same time, they play an important role in studying small-sized systems such as colloidal particles [13], biomolecules [14, 15], and molecular motors [16], where thermal fluctuation effects are important. Further theoretical and experimental studies are found in recent review papers [17, 18].

We are interested in mutual correlations among the thermodynamic quantities. Most studies have been focused on the fluctuations of an individual thermodynamic quantity with a few exceptions [19, 20]. The current study is motivated by our recent work on the modified fluctuation relation for the heat [21]. The amounts of a work \mathcal{W} and a heat \mathcal{Q} during a nonequilibrium process over a time interval Δt are constrained by the thermodynamic first law

$$\mathcal{W} = \mathcal{Q} + \Delta\mathcal{E} \quad (1)$$

where $\Delta\mathcal{E}$ denotes the change in the internal energy of the system. With nonzero net energy flow, both \mathcal{W} and \mathcal{Q} scale with the time interval Δt while their difference $\Delta\mathcal{E}$ does not on average. Hence, one may expect that the heat would follow the same fluctuation theorem obeyed by the work in the large Δt limit. However, various studies found that the fluctuation theorem breaks down for the heat [22, 23, 24, 25, 26, 27, 28, 29, 30]. The breakdown suggests that the effect of the boundary term $\Delta\mathcal{E}$ may persist even in the infinite time limit [31, 32]. Moreover, the modified fluctuation relation for the heat derived in Ref. [21] suggests that the correlation between the heat and the energy change plays an important role in nonequilibrium processes.

Based on this motivation, we investigate the mutual correlations among the thermodynamic quantities in a linear diffusion system. It is simple, but exhibits various nontrivial genuine nonequilibrium phenomena [33, 34, 35]. We develop a path integral formalism to study the joint probability distribution analytically. Our study gives a hint on the reason why the fluctuations of the work and the heat are different.

This paper is organized as follows: In Sec. 2, we introduce an overdamped Langevin dynamics for a nonequilibrium system driven by both a time-dependent perturbation and a nonconservative force, and review the stochastic thermodynamics formalism for

the fluctuation theorem. In Sec. 3, we derive the modified fluctuation relation for the heat in a general setting. In Ref. [21], we only considered a time-independent nonconservative force. We extend the formalism to include a time-dependent driving force. In Sec. 4, we investigate the fluctuations and the correlations in a two-dimensional linear diffusion system in detail. We develop an analytic method in Appendix A, which allows us to calculate the joint probability distributions of the thermodynamic quantities analytically. We find that there is a strong negative correlation between \mathcal{Q} and $\Delta\mathcal{E}$. We conclude the paper with summary in Sec. 5.

2. Stochastic Thermodynamics for Langevin systems

Consider an overdamped dynamics of a nonequilibrium system in thermal contact with a heat bath at temperature T . When there are N degrees of freedom, a configuration is described by an N -dimensional column vector $\mathbf{x} = (x_1, \dots, x_N)^T$. The Langevin equation reads as

$$\dot{\mathbf{x}}(t) = \mathbf{f} + \boldsymbol{\xi}(t) , \quad (2)$$

where \mathbf{f} is a force and $\boldsymbol{\xi} = (\xi_1, \dots, \xi_N)^T$ is a thermal noise satisfying

$$\langle \xi_i(t) \rangle = 0 , \quad \langle \xi_i(t) \xi_j(t') \rangle = 2\beta^{-1} \delta_{ij} \delta(t - t') , \quad (3)$$

with the inverse temperature $\beta \equiv 1/T$. The superscript T denotes the transpose. The damping coefficient and the Boltzmann constant are set to unity. In general, the force $\mathbf{f} = \mathbf{f}(\mathbf{x}, \alpha)$ is a sum of conservative and nonconservative forces as

$$\mathbf{f}(\mathbf{x}, \alpha) = -\nabla_{\mathbf{x}} V(\mathbf{x}, \alpha) + \mathbf{f}_{nc}(\mathbf{x}) \quad (4)$$

with an energy function $V(\mathbf{x}, \alpha)$. The energy function may depend on a time-dependent external parameter $\alpha = \alpha(t)$, called a protocol. The nonconservative force \mathbf{f}_{nc} cannot be written as a gradient of any scalar function.

When $\mathbf{f}_{nc} = 0$ and α is independent of t , the system relaxes into a thermal equilibrium state characterized by the Boltzmann distribution [36, 37]

$$P_{eq}(\mathbf{x}, \alpha) = \exp[\beta F(\alpha) - \beta V(\mathbf{x}, \alpha)] \quad (5)$$

with the free energy given by

$$F(\alpha) = -\beta^{-1} \ln \left[\int d\mathbf{x} e^{-\beta V(\mathbf{x}, \alpha)} \right] . \quad (6)$$

A nonzero \mathbf{f}_{nc} or a time-dependent protocol $\alpha(t)$ drives the system out of equilibrium.

During the time evolution, the system exchanges the energy with the environment. Suppose that the system evolves in time along a stochastic path or trajectory $\mathbf{x}(t)$ during the time interval $t_i \leq t \leq t_f$. Then, the nonequilibrium work done on the system is given by [33, 38]

$$\mathcal{W}[\mathbf{x}(t)] = \int_{t_i}^{t_f} dt \left[\frac{d\alpha}{dt} \frac{\partial V(\mathbf{x}, \alpha)}{\partial \alpha} + \dot{\mathbf{x}}^T \cdot \mathbf{f}_{nc}(\mathbf{x}) \right] , \quad (7)$$

where the first term is the thermodynamic work required to change the external parameter and the second term is the work done by the nonconservative force. The change in the internal energy is given by

$$\Delta\mathcal{E}[\mathbf{x}(t)] = V(\mathbf{x}(t_f), \alpha(t_f)) - V(\mathbf{x}(t_i), \alpha(t_i)). \quad (8)$$

It can be rewritten as

$$\begin{aligned} \Delta\mathcal{E}[\mathbf{x}(t)] &= \int_{t_i}^{t_f} dt \frac{d}{dt} V(\mathbf{x}(t), \alpha(t)) \\ &= \int_{t_i}^{t_f} dt \left[\frac{d\alpha}{dt} \frac{\partial V}{\partial \alpha} + \dot{\mathbf{x}}^T \cdot \nabla_{\mathbf{x}} V \right]. \end{aligned} \quad (9)$$

The heat dissipated into the bath is then given by

$$\mathcal{Q}[\mathbf{x}(t)] = \mathcal{W}[\mathbf{x}(t)] - \Delta\mathcal{E}[\mathbf{x}(t)] = \int_{t_i}^{t_f} dt \dot{\mathbf{x}}^T \cdot \mathbf{f}. \quad (10)$$

Note that the integral in (7), (9), and (10) is the Stratonovich integral [36].

Since the system follows the stochastic Langevin dynamics, thermodynamic quantities \mathcal{W} , $\Delta\mathcal{E}$, and \mathcal{Q} are random variables. Stochastic thermodynamics predicts several interesting identities, known as the fluctuation theorems, for their probability density functions (PDFs). We present a brief summary on the fluctuation theorems [18].

The key feature behind the fluctuation theorem is that the thermodynamic quantity can be written in terms of a relative entropy [39] between the path probabilities in forward (F) and reverse (R) processes. The F process is specified by a protocol $\alpha(t)$, a nonconservative force \mathbf{f}_{nc} , and a PDF P_i for the initial configuration. The R process, corresponding to the F process, is specified by the time-reversed protocol $\alpha^R(t) \equiv \alpha(t_f - (t - t_i))$, the same nonconservative force \mathbf{f}_{nc} , and a PDF P_i^R for the initial configuration. Consider a following quantity associated with a path $\mathbf{x}(t_i \leq t \leq t_f)$

$$\mathcal{Y}[\mathbf{x}(t)] \equiv \ln \left(\frac{\mathcal{P}[\mathbf{x}(t)]}{\mathcal{P}^R[\mathbf{x}^R(t)]} \right), \quad (11)$$

where $\mathcal{P}[\mathbf{x}(t)]$ and $\mathcal{P}^R[\mathbf{x}(t)]$ are the probability distribution of the system following a trajectory $\mathbf{x}(t)$ in the F and R processes, respectively, and $\mathbf{x}^R(t) \equiv \mathbf{x}(t_f - (t - t_i))$ is the time-reversed trajectory. Such a quantity satisfies the identity

$$\langle e^{-\mathcal{Y}[\mathbf{x}(t)]} \rangle = 1, \quad (12)$$

where the average is taken over all paths $\mathbf{x}(t)$ in the F process. The Jensen's inequality then yields that

$$\langle \mathcal{Y}[\mathbf{x}(t)] \rangle \geq 0. \quad (13)$$

The path probability distribution is given by

$$\mathcal{P}^{(R)}[\mathbf{x}(t)] = \mathcal{T}^{(R)}[\mathbf{x}(t)|\mathbf{x}(t_i)] P_i^{(R)}(\mathbf{x}_i) \quad (14)$$

with the conditional probability $\mathcal{T}^{(R)}[\mathbf{x}(t)|\mathbf{x}(t_i)]$ for a path $\mathbf{x}(t)$ starting at $\mathbf{x}(t = t_i)$ in the F (without superscript) and R (with superscript $^{(R)}$) processes. Using the

Onsager-Machlup formalism [40], one can show that the ratio between the conditional probabilities is equal to the heat dissipation [5, 8, 33]:

$$\mathcal{Q}[\mathbf{x}(t)] = \beta^{-1} \ln \left(\frac{\mathcal{T}[\mathbf{x}(t)|\mathbf{x}_i]}{\mathcal{T}^R[\mathbf{x}^R(t)|\mathbf{x}_f]} \right) \quad (15)$$

with $\mathbf{x}_i = \mathbf{x}(t = t_i)$ and $\mathbf{x}_f = \mathbf{x}^R(t = t_i) = \mathbf{x}(t_f)$. Through this relation, \mathcal{Y} can represent a thermodynamic quantity with a suitable choice of P_i and P_i^R . Such a quantity then automatically satisfies the identity of (12), which is referred to as an integral fluctuation theorem (IFT).

One can obtain the well-known ITF for the total entropy change

$$\Delta\mathcal{S} = -\ln \left[\frac{P_f(\mathbf{x}(t_f))}{P_i(\mathbf{x}(t_i))} \right] + \beta\mathcal{Q} \quad (16)$$

by choosing $P_i^R(\mathbf{x})$ as the PDF $P_f(\mathbf{x})$ of finding the system, evolving from the initial PDF $P_i(\mathbf{x})$ at $t = t_i$ in the F process, in configuration \mathbf{x} at time $t = t_f$. The first term corresponds to the change in the Shannon entropy of the system $\Delta\mathcal{S}_{sys}$, while the second term the change of the heat bath entropy.

One can also obtain the ITF for the nonequilibrium work, known as the Jarzynski equality [3], by choosing $P_i(\mathbf{x}) = P_{eq}(\mathbf{x}, \alpha_i = \alpha(t_i))$ and $P_i^R(\mathbf{x}) = P_{eq}(\mathbf{x}, \alpha_f = \alpha(t_f))$ with the Boltzmann distribution in (5). With this choice, one finds that $\mathcal{Y} = \beta(\mathcal{Q} + \Delta\mathcal{E} - \Delta F) = \beta(\mathcal{W} - \Delta F)$ with the free energy difference $\Delta F \equiv F(\alpha_f) - F(\alpha_i)$.

In a certain circumstance, the functional $\mathcal{Y}[\mathbf{x}(t)]$ and the functional $\mathcal{Y}^R[\mathbf{x}^R(t)] \equiv \ln[\mathcal{P}^R[\mathbf{x}(t)]/\mathcal{P}^{RR}[\mathbf{x}^R(t)]]$ may satisfy a relation $\mathcal{Y}^R[\mathbf{x}^R(t)] = -\mathcal{Y}[\mathbf{x}(t)]$. It holds only when the reverse process of the R process is equivalent to the original F process, i.e., $\mathcal{P}^{RR}[\mathbf{x}(t)] = \mathcal{P}[\mathbf{x}(t)]$, which is called an involution property [20]. Then, the PDF $P(Y) \equiv \langle \delta(\mathcal{Y}[\mathbf{x}(t)] - Y) \rangle$ for the F process and the PDF $P_R(Y) \equiv \langle \delta(\mathcal{Y}^R[\mathbf{x}^R(t)] - Y) \rangle_R$ for the R process satisfy the identity [8]

$$\frac{P(Y)}{P_R(-Y)} = e^Y, \quad (17)$$

which is called a detailed fluctuation theorem (DFT) in comparison to the IFT. The DFT implies the IFT, while the converse is not true in general. Using (11) and the involution property, one can derive (17) as follows:

$$\begin{aligned} P(Y) &= \int [D\mathbf{x}] \delta(\mathcal{Y}[\mathbf{x}] - Y) \mathcal{P}[\mathbf{x}] \\ &= \int [D\mathbf{x}] \delta(\mathcal{Y}[\mathbf{x}] - Y) \mathcal{P}^R[\mathbf{x}^R] e^{\mathcal{Y}[\mathbf{x}]} \\ &= \int [D\mathbf{x}^R] \delta(-\mathcal{Y}^R[\mathbf{x}^R] - Y) \mathcal{P}^R[\mathbf{x}^R] e^{-\mathcal{Y}^R[\mathbf{x}^R]} \\ &= e^Y P_R(-Y), \end{aligned}$$

where $\int [D\mathbf{x}]$ denotes the path integral.

The choice of $P_i(\mathbf{x}) = P_{eq}(\mathbf{x}, \alpha_i)$ and $P_i^R(\mathbf{x}) = P_{eq}(\mathbf{x}, \alpha_f)$ leading to $\mathcal{Y} = \beta(\mathcal{W} - \Delta F)$ preserves the involution property. Hence, $\beta(\mathcal{W} - \Delta F)$ satisfies the DFT, which is referred to as the Crooks fluctuation theorem [4].

The total entropy production $\Delta\mathcal{S}$ corresponds to the choice of $P_i^R(\mathbf{x}) = P_f(\mathbf{x})$. In general nonequilibrium systems, the PDF $P_f(\mathbf{x})$ does return to the original PDF $P_i(\mathbf{x})$ under the R process. Hence, the total entropy production does not obey the DFT. There is an exceptional case. Suppose that the external parameter α is a time-independent constant and the system is in the nonequilibrium steady state initially. Then, the system remains at the steady state at all times and the involution property holds. Hence, the entropy production in the nonequilibrium steady state obeys the DFT.

Note that the functional in (11) is the relative entropy of two probability distributions \mathcal{P} and \mathcal{P}^R . One may adopt the path probability distribution from a different dynamics in (11) instead of the R process. For example, if one chooses the so-called dual or adjoint dynamics, then the heat can be decomposed into two parts as $\mathcal{Q} = \mathcal{Q}_{ex} + \mathcal{Q}_{hk}$ [7, 9]. When a system is in a nonequilibrium steady state, it gains a work done by \mathbf{f}_{nc} and dissipates the same amount of a heat into the heat bath. The house-keeping heat \mathcal{Q}_{hk} refers to the heat necessary to maintain the nonequilibrium steady state. The excess heat \mathcal{Q}_{ex} refers to the heat dissipated in transient dynamics [7]. As well as the total entropy production $\Delta\mathcal{S} = \Delta\mathcal{S}_{sys} + \beta\mathcal{Q}_{ex} + \beta\mathcal{Q}_{hk}$, each of $\Delta\mathcal{S}_{sys} + \beta\mathcal{Q}_{ex}$ and $\beta\mathcal{Q}_{hk}$ is known to satisfy the IFT, respectively [9]. The total heat may be decomposed in a different way for underdamped systems [11, 12], which is not covered in the paper.

3. Modified fluctuation relation for heat

It is an interesting question whether the heat also satisfies the fluctuation theorem. A careful consideration of (11) provides an example with the affirmative answer. If one chooses the uniform distribution for P_i and P_i^R , the functional \mathcal{Y} becomes equal to $\beta\mathcal{Q}$. In this case, the heat can satisfy the fluctuation theorem. However, this is a peculiar case since the uniform distribution cannot be realized in systems whose phase space is unbounded. So the main question is whether the heat satisfies the fluctuation theorem in systems following the equilibrium Boltzmann distribution initially.

Theoretical and experimental studies have shown that the heat, unlike the work, does not obey the fluctuation theorem even in the infinite $\Delta t = t_f - t_i$ limit [23, 24, 25]. It is rather surprising because the work and the heat are proportional to Δt on average while their difference $\langle\mathcal{W}\rangle - \langle\mathcal{Q}\rangle = \langle\Delta\mathcal{E}\rangle$ does not scale with Δt . The breakdown is attributed to a rare but large fluctuation of the system in the energy landscape [30].

Recently, a general relation, called the modified fluctuation relation, was found for the heat [21]. It was derived for systems only with a nonconservative force. Here we generalize it to cover the systems driven by both a time-dependent protocol $\alpha(t)$ and a nonconservative force.

The system starts from the Boltzmann distribution of (5) with $\alpha = \alpha_i$ (α_f) in the F (R) process so that the functional in (11) becomes as $\mathcal{Y}[\mathbf{x}] = \ln(\mathcal{P}[\mathbf{x}]/\mathcal{P}^R[\mathbf{x}^R]) = \beta(\mathcal{Q}[\mathbf{x}] + \Delta\mathcal{E}[\mathbf{x}] - \Delta F)$. We rewrite it as a relation between the path probabilities in the F and R processes:

$$\mathcal{P}[\mathbf{x}] = e^{\beta(\mathcal{Q}[\mathbf{x}] + \Delta\mathcal{E}[\mathbf{x}] - \Delta F)} \mathcal{P}^R[\mathbf{x}^R] . \quad (18)$$

Multiplying both sides with $\delta(\mathcal{Q}[\mathbf{x}] - Q)\delta(\Delta\mathcal{E}[\mathbf{x}] - E)$ and integrating over all paths, we obtain the fluctuation theorem

$$P_{\text{he}}(Q, E) = e^{\beta(Q+E-\Delta F)} P_{\text{he}}^R(-Q, -E) . \quad (19)$$

for the joint PDF of the heat and the energy change defined as

$$P_{\text{he}}(Q, E) \equiv \langle \delta(\mathcal{Q}[\mathbf{x}] - Q)\delta(\Delta\mathcal{E}[\mathbf{x}] - E) \rangle . \quad (20)$$

In deriving (19), we have used that $\mathcal{Q}^R[\mathbf{x}^R] = -\mathcal{Q}[\mathbf{x}]$, $\Delta\mathcal{E}^R[\mathbf{x}^R] = -\Delta\mathcal{E}[\mathbf{x}]$, and $\int[D\mathbf{x}] = \int[D\mathbf{x}^R]$. The fluctuation theorem for the joint PDF was also considered in Ref. [19, 20].

Hereafter, we will use ‘h’, ‘w’, and ‘e’ in the subscript for a PDF of a heat, work, and energy change, respectively. When there are multiple subscripts as in (20), it should be understood as a joint PDF of corresponding quantities. In addition, we will use a ‘|’ in the subscript for a conditional PDF. For example, $P_{\text{elh}}(E|Q)$ denotes the conditional probability that the energy change is E given that the heat dissipation is Q .

The marginal distribution of the heat is given by $P_{\text{h}}(Q) = \int dE P_{\text{he}}(Q, E)$. Integrating both sides of (19) over E , we obtain that

$$P_{\text{h}}(Q) = e^{\beta(Q-\Delta F)} \left(\int dE P_{\text{he}}^R(-Q, -E) e^{\beta E} \right) . \quad (21)$$

The term in the parenthesis is simplified by using the conditional probability $P_{\text{elh}}(E|Q) = P_{\text{he}}(Q, E)/P_{\text{h}}(Q)$. It leads to the relation

$$\frac{P_{\text{h}}(Q)}{P_{\text{h}}^R(-Q)} = e^{\beta(Q-\Delta F)} \Psi^R(-Q) . \quad (22)$$

where

$$\Psi^R(Q) \equiv \int dE e^{-\beta E} P_{\text{elh}}^R(E|Q) . \quad (23)$$

Applying the relation (22) to the R process and using the involution property that the reverse process of the R process is equivalent to the F process, one can show that

$$\Psi^R(-Q) = 1/\Psi(Q) \quad (24)$$

where

$$\Psi(Q) \equiv \int dE e^{-\beta E} P_{\text{elh}}(E|Q) . \quad (25)$$

Therefore, we obtain the modified fluctuation relation for the heat

$$\frac{P_{\text{h}}(Q)}{P_{\text{h}}^R(-Q)} = e^{\beta(Q-\Delta F)} / \Psi(Q) . \quad (26)$$

Being compared with the DFT in (17), the modified fluctuation relation is dressed by the additional factor $1/\Psi(Q) = \Psi^R(-Q)$. In order to check whether the heat satisfies the IFT in (12), we evaluate $\langle e^{-\beta\mathcal{Q}[\mathbf{x}]} \rangle$ using (18) and (19). It yields that

$$\left\langle e^{-\beta(\mathcal{Q}[\mathbf{x}]-\Delta F)} \right\rangle = \left\langle e^{-\beta\Delta\mathcal{E}^R[\mathbf{x}]} \right\rangle_R . \quad (27)$$

It is also dressed by the additional factor representing the fluctuation of the energy change in the R process.

The additional factor $\Psi(Q)$ in (26) reflects a correlation between the heat and the energy change during a nonequilibrium process. This calls for the study of mutual correlations between thermodynamic quantities as well as their individual fluctuations. The energy change, the work, and the heat are constrained by the thermodynamic first law in (1). So, it suffices to specify a single joint PDF, e.g., $P_{\text{we}}(W, E)$. The other joint PDFs are given by

$$P_{\text{he}}(Q, E) = P_{\text{we}}(Q + E, E) \quad (28)$$

and

$$P_{\text{wh}}(W, Q) = P_{\text{we}}(W, W - Q) , \quad (29)$$

from which the marginal distributions $P_{\text{w}}(W)$, $P_{\text{h}}(Q)$, and $P_{\text{e}}(E)$ are obtained.

It is convenient to deal with the moment generating functions (MGFs). We will use the symbol G to denote a MGF, and adopt the same subscript notation for the MGF as that for the PDF. Parameters λ , κ , and η will be used as the conjugate variables for the work, the energy change, and the heat, respectively. For example, $G_{\text{we}}(\lambda, \kappa)$ stands for the MGF defined as

$$G_{\text{we}}(\lambda, \kappa) \equiv \int dQ \int dE P_{\text{we}}(W, E) e^{-\beta(\lambda W + \kappa E)} . \quad (30)$$

It is easy to show that the other MGFs for the joint PDFs are given by

$$G_{\text{he}}(\eta, \kappa) = G_{\text{we}}(\eta, -\eta + \kappa) \quad (31)$$

and

$$G_{\text{wh}}(\lambda, \eta) = G_{\text{we}}(\lambda + \eta, -\eta) . \quad (32)$$

The MGFs for the marginal distributions are given by $G_{\text{w}}(\lambda) = G_{\text{we}}(\lambda, 0)$, $G_{\text{e}}(\kappa) = G_{\text{we}}(0, \kappa)$, and $G_{\text{h}}(\eta) = G_{\text{we}}(\eta, -\eta)$.

In terms of the MGF, the DFT or the Crooks fluctuation theorem for the work can be written as

$$G_{\text{w}}(\lambda) = e^{-\beta\Delta F} G_{\text{w}}^R(1 - \lambda) . \quad (33)$$

or

$$G_{\text{we}}(\lambda, 0) = e^{-\beta\Delta F} G_{\text{we}}^R(1 - \lambda, 0) . \quad (34)$$

The modified fluctuation relation for the heat in (26) can be rewritten as

$$G_{\text{he}}(\eta, 0) = e^{-\beta\Delta F} G_{\text{he}}^R(1 - \eta, 1) . \quad (35)$$

In comparison with (34), the heat fluctuation deviates from the DFT by the factor $G_{\text{he}}^R(1 - \eta, 1)/G_{\text{he}}^R(1 - \eta, 0)$.

4. Linear diffusion system

In this section, we investigate an exactly solvable two-dimensional linear diffusion system. Fluctuations and correlations are studied in detail to demonstrate the fluctuation theorems for the joint PDF and the modified fluctuation relation for the heat. Especially, we focus on the question whether the DFT for the heat holds asymptotically in the infinite time-interval limit or not.

We investigate the nonequilibrium fluctuations in a system exerted by a linear force [33, 34]

$$\mathbf{f}(\mathbf{x}) = -\mathbf{F} \cdot \mathbf{x} \quad (36)$$

with a time-independent force matrix \mathbf{F} . The force is given by the sum of a conservative force $\mathbf{f}_c(\mathbf{x}) = -\mathbf{F}_s \cdot \mathbf{x}$ and a nonconservative force $\mathbf{f}_{nc}(\mathbf{x}) = -\mathbf{F}_a \cdot \mathbf{x}$ with the symmetric component $\mathbf{F}_s = (\mathbf{F} + \mathbf{F}^T)/2$ and the anti-symmetric component $\mathbf{F}_a = (\mathbf{F} - \mathbf{F}^T)/2$ [41]. The conservative force is also written as $\mathbf{f}_c(\mathbf{x}) = -\mathbf{F}_s \cdot \mathbf{x} = -\nabla_{\mathbf{x}} V(\mathbf{x})$ with the energy function $V(\mathbf{x}) \equiv \frac{1}{2} \mathbf{x}^T \cdot \mathbf{F}_s \cdot \mathbf{x}$. The work, heat, and energy change for a path $\mathbf{x}(t_i \leq t \leq t_f)$ are given by

$$\mathcal{W}[\mathbf{x}] = - \int_{t_i}^{t_f} dt \dot{\mathbf{x}}^T(t) \cdot \mathbf{F}_a \cdot \mathbf{x}(t) \quad (37)$$

$$\mathcal{Q}[\mathbf{x}] = - \int_{t_i}^{t_f} dt \dot{\mathbf{x}}^T(t) \cdot \mathbf{F} \cdot \mathbf{x}(t) \quad (38)$$

$$\Delta \mathcal{E}[\mathbf{x}] = \frac{1}{2} \mathbf{x}_f^T \cdot \mathbf{F}_s \cdot \mathbf{x}_f - \frac{1}{2} \mathbf{x}_i^T \cdot \mathbf{F}_s \cdot \mathbf{x}_i \quad (39)$$

where the integral is of Stratonovich type, $\mathbf{x}_i = \mathbf{x}(t_i)$, and $\mathbf{x}_f = \mathbf{x}(t_f)$. Without time-dependent driving force, the \mathbf{F} and \mathbf{R} processes are the same and $\Delta F = 0$. Hereafter, the energy will be measured in unit of $k_B T$ and the temperature be set to unity. The system is assumed to be in the equilibrium state with the Boltzmann distribution given in (5) initially.

The linear system covers a wide range of physical systems such as a colloidal particle trapped in an optical tweezer [13, 23, 24], harmonic networks [42, 43, 44, 45], and RC circuits [25, 46]. In a linear diffusion system [33, 34], the equilibrium relaxation dynamics and the nonequilibrium driven dynamics are competing with each other. The competition leads to an intriguing dynamical behavior. For instance, a two-dimensional linear diffusion system undergoes multiple locking-unlocking dynamical transitions with time in the tail shape of $P_w(W)$ [34].

In this work, we consider a simplest force matrix in two dimensions:

$$\mathbf{F} = \begin{pmatrix} 1 & \varepsilon \\ -\varepsilon & 1 \end{pmatrix} = \mathbf{I} + i\varepsilon \sigma_y \quad (40)$$

with the identity matrix \mathbf{I} and the y component of the Pauli matrix σ_y . With this force matrix, the two-dimensional linear diffusion system describes a particle trapped in an isotropic harmonic potential $V(\mathbf{x}) = (x_1^2 + x_2^2)/2$ and driven by a swirling nonconservative force $\mathbf{f}_{nc} = -i\varepsilon \sigma_y \cdot \mathbf{x}$ of strength ε . This system does not exhibit the locking-unlocking

transition observed in a system with an anisotropic harmonic potential [34]. Yet, it displays nontrivial correlations between thermodynamic quantities.

In a linear diffusion system, the work fluctuation can be studied by using the path integral formalism developed in Ref. [33]. We generalize the formalism to cover the joint PDF, which is explained in Appendix A. The formal solution for the MGF $G_{\text{we}}(\lambda, \kappa)$ is given in (A.8). To obtain the explicit solution, one needs to solve the differential equation in (A.4) for $\tilde{\mathbf{A}}(t)$ with the initial condition

$$\tilde{\mathbf{A}}(t = t_i) = (1 - \kappa)\mathbf{I} . \quad (41)$$

For convenience, we will set $t_i = 0$ hereafter.

The auxiliary matrices in (A.4) is given by $\tilde{\mathbf{F}} = \mathbf{I} + i\varepsilon(1 - 2\lambda)\sigma_y$ and $\mathbf{\Lambda} = 2\varepsilon^2\lambda(1 - \lambda)\mathbf{I}$. The off-diagonal elements of $\tilde{\mathbf{F}}$ are anti-symmetric and $\mathbf{\Lambda} \propto \mathbf{I}$. Hence, $\tilde{\mathbf{A}}(t)$, starting from the initial condition in (41), is proportional to the identity matrix at all t . Substituting $\tilde{\mathbf{A}}(t)$ with $z(t)\mathbf{I}$ in (A.4), one obtains a differential equation for $z(t)$:

$$\dot{z} = -2z^2 + 2z + 2\varepsilon^2\lambda(1 - \lambda) \quad (42)$$

with $z(0) = (1 - \kappa)$. The solution is given by

$$z(t) = \frac{1}{2} \left(1 + \frac{(1 - 2\kappa) + \Omega(\lambda) \tanh(\Omega(\lambda)t)}{1 + \frac{(1 - 2\kappa)}{\Omega(\lambda)} \tanh(\Omega(\lambda)t)} \right) \quad (43)$$

with

$$\Omega(\lambda) = \sqrt{1 - 4\varepsilon^2\lambda(\lambda - 1)} . \quad (44)$$

Inserting the solution into (A.8), one obtains

$$G_{\text{we}}(\lambda, \kappa) = B(\lambda, \kappa) , \quad (45)$$

where the function $B(x, y)$ is defined as

$$B(x, y) \equiv \frac{e^t}{\cosh(\Omega(x)t) + \frac{(1 - 4y^2) + \Omega(x)^2}{2\Omega(x)} \sinh(\Omega(x)t)} . \quad (46)$$

It is symmetric under $x \rightarrow 1 - x$ and $y \rightarrow -y$. Note that it diverges when the denominator vanishes. We plot the lines of singularity at $t = 1$ (solid line) and $t = \infty$ (dashed line) in the $\lambda - \kappa$ plane in Fig. 1. The solid line is obtained numerically. Taking $t \rightarrow \infty$ limit in (46), one finds that the dashed line is parameterized as $(\Omega(\lambda) - 1)^2 = 4\kappa^2$. It consists of the curved segments $\kappa = \pm(\Omega(\lambda) - 1)/2$ for $\lambda_-^* \leq \lambda \leq \lambda_+^*$ and $|\kappa| \geq 1/2$, and the linear segments $\lambda = \lambda_{\pm}^*$ for $|\kappa| < 1/2$, where

$$\lambda_{\pm}^* = \frac{1}{2} \pm \frac{\sqrt{1 + \varepsilon^2}}{2\varepsilon} . \quad (47)$$

The singularity provides an information on the asymptotic tail behavior of the probability distribution [22, 26], which will be analyzed further.

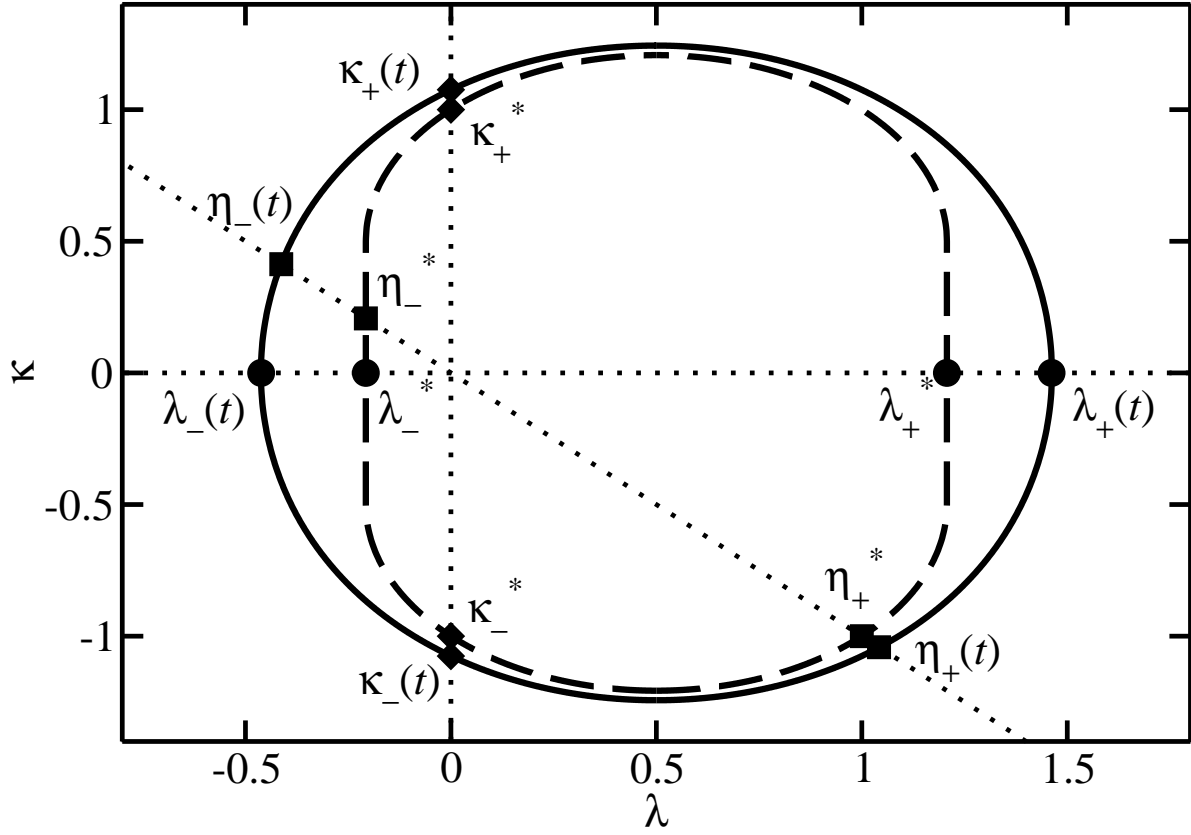


Figure 1. Line of singularity of $B(\lambda, \kappa)$ at $t = 1$ (solid line) and $t = \infty$ (dashed line).

4.1. Fluctuations of work

The MGF of the work is given by

$$G_w(\lambda) = G_{we}(\lambda, 0) = B(\lambda, 0) . \quad (48)$$

The symmetry property of the function B ensures the DFT in (33) with $\Delta F = 0$. The mean value of the work is given by

$$\langle \mathcal{W} \rangle = - \left. \frac{dG_w(\lambda)}{d\lambda} \right|_{\lambda=0} = 2\varepsilon^2 t . \quad (49)$$

It grows linearly with time t . That is, the driving force \mathbf{f}_{nc} performs a work at the uniform rate $2\varepsilon^2$.

At a given value of t , $G_w(\lambda)$ has simple poles at $\lambda_+(t) > 1$ and $\lambda_-(t) < 0$, which are marked with the closed circles in Fig. 1. Due to the symmetry $G_w(\lambda) = G_w(1 - \lambda)$, $\lambda_+(t) + \lambda_-(t) = 1$. The simple poles indicate exponential tails in $P_w(W)$:

$$P_w(W) \sim \begin{cases} e^{\lambda_+(t)W} & , \quad W \ll -1 , \\ e^{\lambda_-(t)W} & , \quad W \gg 1 . \end{cases} \quad (50)$$

The tail shape of $P_w(W)$ can be characterized more quantitatively by the large deviation functions (LDFs) [47] defined as

$$\pi_w(w) \equiv - \lim_{t \rightarrow \infty} \frac{1}{t} \ln P_w(W = wt) , \quad (51)$$

$$\gamma_w(\lambda) \equiv - \lim_{t \rightarrow \infty} \frac{1}{t} \ln G_w(\lambda) . \quad (52)$$

The symbol π (γ) is used to denote the LDF for the PDF (MGF). They are related through the Legendre transformation

$$\pi_w(w) = \max_{\lambda} \{ \gamma_w(\lambda) - \lambda w \} . \quad (53)$$

By taking the $t \rightarrow \infty$ limit of (48), we obtain that

$$\gamma_w(\lambda) = \begin{cases} \Omega(\lambda) - 1 & , \quad \lambda_-^* < \lambda < \lambda_+^* \\ -\infty & , \quad \text{otherwise} \end{cases} . \quad (54)$$

So the Legendre transformation yields that

$$\pi_w(w) = \sqrt{\frac{(1 + \varepsilon^2)(w^2 + 4\varepsilon^2)}{4\varepsilon^2}} - \frac{w}{2} - 1 . \quad (55)$$

It has the limiting behavior $\pi_w(w \rightarrow \pm\infty) \simeq -\lambda_{\mp}^* w$, which is consistent with the exponential tails in (50). In terms of the LDF, the DFT for the work is written as $\gamma_w(\lambda) = \gamma_w(1 - \lambda)$ and $\pi_w(w) - \pi_w(-w) = -w$. The explicit solutions in (54) and (55) confirm the DFT.

4.2. Fluctuations of energy change

The MGF of the energy change is given by

$$G_e(\kappa) = G_{we}(0, \kappa) = B(0, \kappa) . \quad (56)$$

It also has simple poles at $\kappa = \kappa_{\pm}(t)$ with $\kappa_{\pm}^* = \lim_{t \rightarrow \infty} \kappa_{\pm}(t) = \pm 1$, which are marked with the closed diamonds in Fig. 1. The simple poles indicate that $P_e(E) \sim e^{\kappa_{\mp}(t)E}$ for large $|E|$. One can obtain $P_e(E)$ exactly from the Fourier transform

$$P_e(E) = \int_{-\infty}^{\infty} \frac{d\kappa}{2\pi} e^{i\kappa E} G_e(i\kappa) = \frac{e^{-|E|/\sqrt{1-e^{-2t}}}}{2\sqrt{1-e^{-2t}}} . \quad (57)$$

It indeed decays exponentially. The LDF is given by

$$\pi_e(e) = |e| . \quad (58)$$

The energy change is distributed symmetrically. So, the system may gain or lose the energy equally probably. It is interesting to note that the PDF is independent of the driving strength ε . The independence is due to a specific property of the force matrix in (40). The nonconservative force $\mathbf{f}_{nc} = i\varepsilon\sigma_y \cdot \mathbf{x}$ is perpendicular to the conservative force $\mathbf{f}_c = -\nabla V(\mathbf{x}) = -\mathbf{x}$. Hence the nonequilibrium force does not affect the energy fluctuation.

4.3. Fluctuations of heat

The MGF of the heat is given by

$$G_h(\eta) = G_{he}(\eta, \kappa = 0) = B(\eta, -\eta) . \quad (59)$$

It has simple poles at $\eta = \eta_{\pm}(t)$, which are marked with closed squares in Fig. 1. From the $t \rightarrow \infty$ limit of (59), the LDF is given by

$$\gamma_h(\eta) = \begin{cases} \Omega(\eta) - 1 & , \quad \eta_-^* < \eta < \eta_+^* \\ -\infty & , \quad \text{otherwise} \end{cases} \quad (60)$$

where

$$\eta_+^* = 1 \quad (61)$$

and

$$\eta_-^* = \begin{cases} -(1 - \varepsilon^2)/(1 + \varepsilon^2) & , \quad \varepsilon^2 \leq 1/3 \\ -\frac{1}{2}(\sqrt{1 + 1/\varepsilon^2} - 1) & , \quad \varepsilon^2 > 1/3 \end{cases} \quad (62)$$

Note that $\gamma_h(\eta)$ has the same function form as $\gamma_w(\lambda)$, but γ_h is supported in the narrower domain. We compare the two LDFs in Fig. 2(a) and (b).

It is straightforward to obtain the LDF $\pi_h(q)$ from the Legendre transformation $\pi_h(q) = \max_{\eta} \{\gamma_h(\eta) - \eta q\}$:

$$\pi_h(q) = \begin{cases} -q & , \quad q < q_+^* \\ \sqrt{\frac{(1+\varepsilon^2)(q^2+4\varepsilon^2)}{4\varepsilon^2}} - \frac{q}{2} - 1 & , \quad q_+^* \leq q \leq q_-^* \\ \frac{1-\varepsilon^2}{1+\varepsilon^2}q - \frac{4\varepsilon^2}{1+\varepsilon^2} & , \quad q_-^* < q \end{cases} \quad (63)$$

where

$$q_+^* = \left. \frac{d\gamma_h(\eta)}{d\eta} \right|_{\eta=\eta_+^*} = -2\varepsilon^2 \quad (64)$$

and

$$q_-^* = \left. \frac{d\gamma_h(\eta)}{d\eta} \right|_{\eta=\eta_-^*} = \begin{cases} 2\varepsilon^2 \frac{(3-\varepsilon^2)}{(1-3\varepsilon^2)} & , \quad \varepsilon^2 < 1/3 \\ \infty & , \quad \varepsilon^2 \geq 1/3 . \end{cases} \quad (65)$$

The LDF for the heat is compared with that of the work in Fig. 2(c) and (d). They deviate from each other at large values of $|w|$ and $|q|$. The heat exhibits stronger fluctuations than the work.

We test whether the LDF of the heat satisfies the DFT. The modified fluctuation relation in (26) is rewritten as

$$\pi_h(q) - \pi_h(-q) = -q - \psi(q) \quad (66)$$

where

$$\psi(q) \equiv -\lim_{t \rightarrow \infty} \frac{1}{t} \ln \Psi(qt) \quad (67)$$

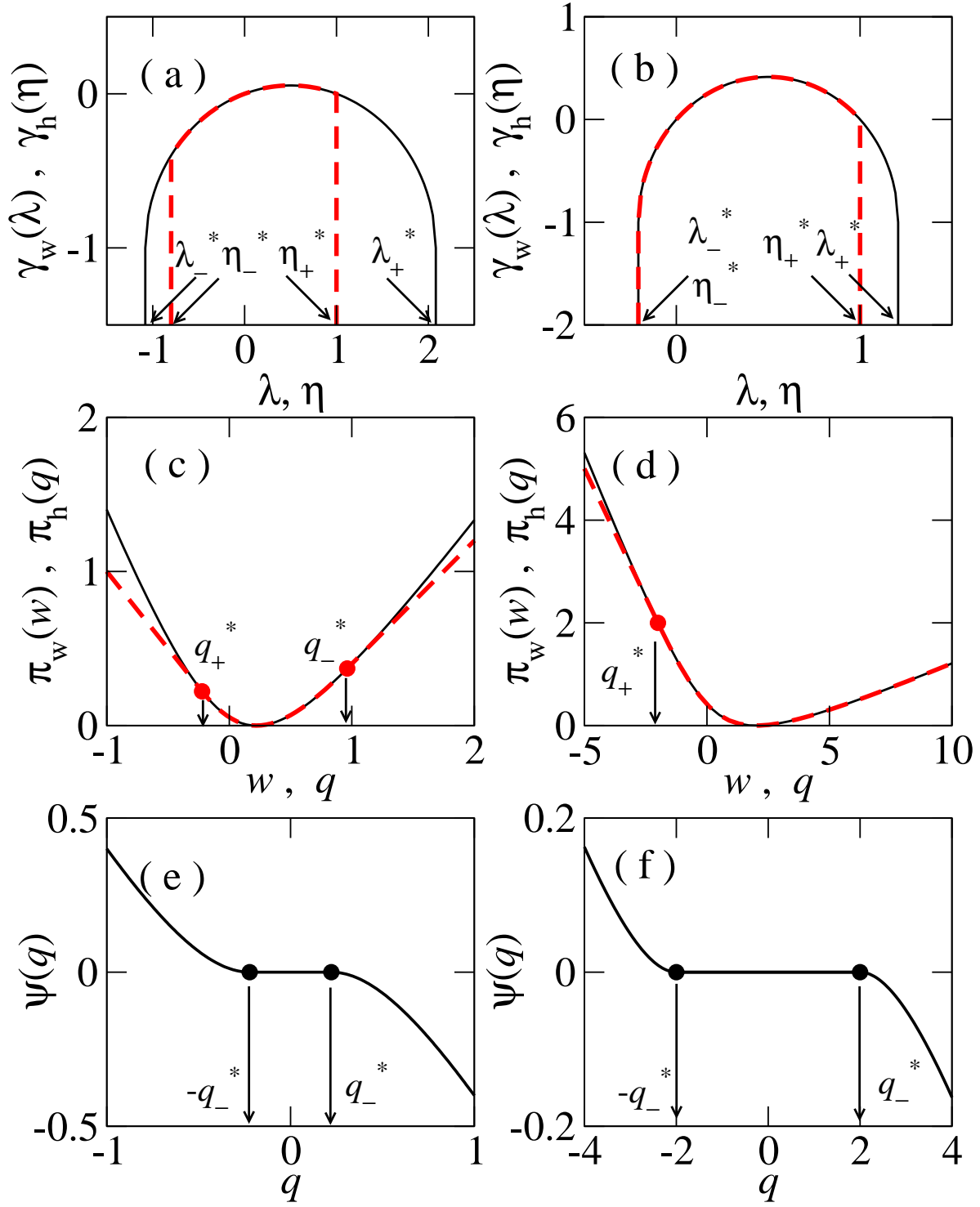


Figure 2. (Color online) LDFs for the MGFs in (a) and (b) and for the PDFs in (c) and (d). Solid and dashed lines are for the work and the heat, respectively. The panels (e) and (f) show the plot of $\psi(q)$. The parameter values are $\varepsilon = 1/3$ in (a), (c), and (e), and $\varepsilon = 1$ in (b), (d), and (f).

with $\Psi(Q)$ in (25). Using (63), we find that

$$\psi(q) = \begin{cases} 0 & , \quad 0 \leq q < -q_+^* \\ \frac{q}{2} - \frac{\sqrt{(1+\varepsilon^2)(q^2+4\varepsilon^2)}}{2\varepsilon} + 1 & , \quad -q_+^* \leq q < q_-^* \\ -\frac{1-\varepsilon^2}{1+\varepsilon^2}q + \frac{4\varepsilon^2}{1+\varepsilon^2} & , \quad q_-^* \leq q \end{cases} \quad (68)$$

and $\psi(-q) = -\psi(q)$. It is plotted in Fig. 2(e) and (f). The heat appears to obey the DFT with $\psi(q) = 0$ within the interval $|q| \leq |q_+^*|$. However, rare fluctuations with large values of $|q|$ do not obey the fluctuation theorem.

4.4. Correlations between thermodynamic quantities

We have shown that the heat does not obey the DFT even in the $t \rightarrow \infty$ limit. The correction factor $\psi(q)$ calculated in (68) does not vanish in the large $|q|$ region. Note that $\Psi(Q) \sim e^{-t\psi(Q/t)}$ reflects the mutual correlation between the heat and the energy change in nonequilibrium dynamics. In this subsection, we investigate the mutual correlations among them.

The LDF for the joint distribution of \mathcal{W} and $\Delta\mathcal{E}$ is defined by

$$\gamma_{\text{we}}(\lambda, \kappa) \equiv - \lim_{t \rightarrow \infty} \frac{1}{t} \ln G_{\text{we}}(\lambda, \kappa) , \quad (69)$$

$$\pi_{\text{we}}(w, e) = - \lim_{t \rightarrow \infty} \frac{1}{t} P_{\text{we}}(W = wt, E = et) . \quad (70)$$

Using the expression in (45) and the analytic property of the function B defined in (46), we obtain that

$$\gamma_{\text{we}}(\lambda, \kappa) = \begin{cases} \Omega(\lambda) - 1 & , \quad (\lambda, \kappa) \in \mathcal{D}_{\text{we}} \\ -\infty & , \quad \text{otherwise} \end{cases} \quad (71)$$

where $\mathcal{D}_{\text{we}} \equiv \{(\lambda, \kappa) | \lambda_-^* < \lambda < \lambda_+^*, |\kappa| < \frac{\Omega(\lambda)+1}{2}\}$ denotes the domain bounded by the dashed line in Fig. 1. The Legendre transformation

$$\pi_{\text{we}}(w, e) = \max_{(\lambda, \kappa) \in \mathcal{D}_{\text{we}}} \{\gamma_{\text{we}}(\lambda, \kappa) - \lambda w - \kappa e\} \quad (72)$$

yields that

$$\pi_{\text{we}}(w, e) = \sqrt{\frac{(1+\varepsilon^2)(w^2 + \varepsilon^2(2+|e|)^2)}{4\varepsilon^2}} - \frac{w - |e|}{2} - 1 . \quad (73)$$

It is minimum at $(w, e) = (2\varepsilon^2, 0)$ and increases linearly in $|q|$ and $|e|$ asymptotically.

The joint distribution of \mathcal{Q} and $\Delta\mathcal{E}$ is related to that of \mathcal{W} and $\Delta\mathcal{E}$ through (28) and (31). Hence, the LDFs $\gamma_{\text{he}}(\eta, \kappa)$ for $G_{\text{he}}(\eta, \kappa)$ and $\pi_{\text{he}}(q, e)$ for $P_{\text{he}}(Q, E)$ are given by

$$\gamma_{\text{he}}(\eta, \kappa) = \gamma_{\text{we}}(\eta, \kappa - \eta) , \quad (74)$$

$$\pi_{\text{he}}(q, e) = \pi_{\text{we}}(q + e, e) . \quad (75)$$

We compare $\pi_{\text{we}}(w, e)$ and $\pi_{\text{he}}(q, e)$ at $\varepsilon = 1/3$ with the density plot in Fig. 3. Interestingly, $\pi_{\text{we}}(w, e) = \pi_{\text{we}}(w, -e)$ at all values of w . Irrespective of an external work,

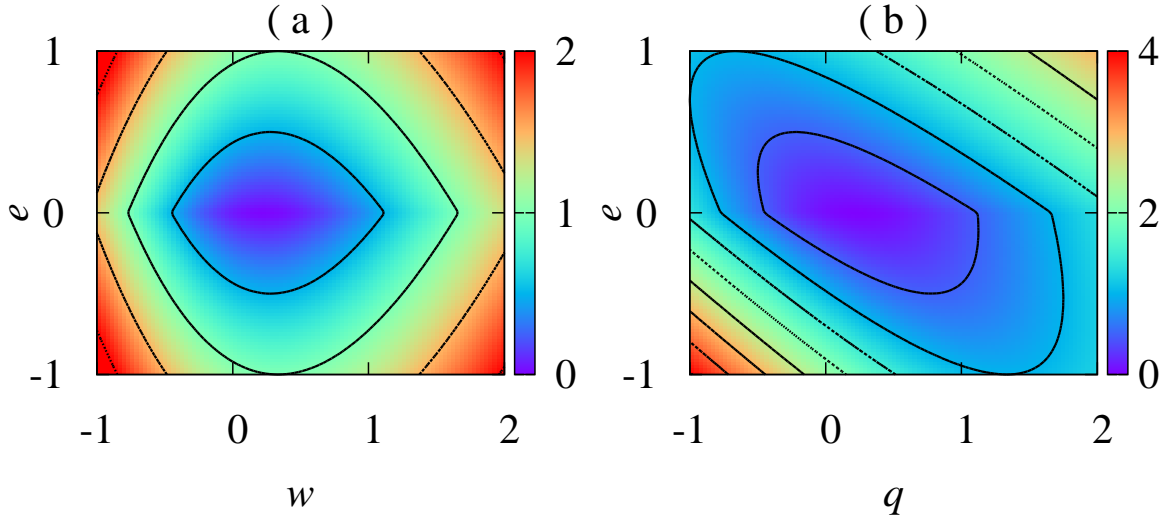


Figure 3. (Color online) Density plots for the LDFs $\pi_{we}(w, e)$ in (a) and $\pi_{he}(q, e)$ in (b) at $\varepsilon = 1/3$. Also drawn are the equiprobable lines.

the internal energy of the system may increase or decrease with the equal probability. By contrast, a strong anti-correlation exists between the heat dissipation and the energy change. The system tends to lose an internal energy when it dissipates a heat and to gain an internal energy when it absorbs a heat.

The mutual correlation is represented well by the most probable value of the energy change $e_{pr}(q)$ to a given value of q . That is to say, $\pi_{he}(q, e)$ is minimum at $e = e_{pr}(q)$ when it is regarded as a function of e with fixed q . Using the explicit solution for $\pi_{he}(q, e)$ in (73) and (75), we find that

$$e_{pr}(q) = \begin{cases} -\frac{q+2\varepsilon^2}{1+\varepsilon^2} & , \quad q < q_+^* \\ 0 & , \quad q_+^* \leq q < q_-^* \\ \frac{-(1-3\varepsilon^2)q+2\varepsilon^2(3-\varepsilon^2)}{1-\varepsilon^4} & , \quad q > q_-^* \end{cases} \quad (76)$$

It takes a positive value for $q < q_+^*$ (< 0) and a negative value for $q > q_-^*$ (> 0).

We will show that the nonzero $e_{pr}(q)$ is directly related to the breakdown of the DFT for the heat. The DFT can be examined by checking whether the relation $\pi_h(q) - \pi_h(-q) = -q$ holds or not. Note that $P_h(Q) = \int dE P_{he}(Q, E) \sim \int de \exp[-t\pi_{he}(Q/t, e)] \sim \exp[-t \min_e \{\pi_{he}(Q/t, e)\}]$, which yields that $\pi_h(q) = \pi_{he}(q, e_{pr}(q))$. Then, it follows that

$$\begin{aligned} \pi_h(q) - \pi_h(-q) &= \pi_{he}(q, e_{pr}(q)) - \pi_{he}(-q, e_{pr}(-q)) \\ &= \pi_{he}(q, 0) - \pi_{he}(-q, 0) \\ &\quad + [\pi_{he}(q, e_{pr}(q)) - \pi_{he}(q, 0)] \\ &\quad - [\pi_{he}(-q, e_{pr}(-q)) - \pi_{he}(-q, 0)] . \end{aligned}$$

Comparing this relation with (66) and using $\pi_{he}(q, 0) - \pi_{he}(-q, 0) = \pi_{we}(q, 0) -$

$\pi_{\text{wr}}(-q, 0) = -q$, we obtain an alternative expression for $\psi(q)$:

$$\begin{aligned} \psi(q) = & [\pi_{\text{he}}(q, e_{pr}(q)) - \pi_{\text{he}}(q, 0)] \\ & - [\pi_{\text{he}}(-q, e_{pr}(-q)) - \pi_{\text{he}}(-q, 0)] . \end{aligned} \quad (77)$$

It would vanish if $e_{pr}(q)$ were equal to 0 at all q . The negative correlation between the heat and the energy change leads to nonzero values of $e_{pr}(q)$, hence nonzero values of $\psi(q)$. This analysis shows that the correlation is the origin of the breakdown of the DFT for the heat.

5. Summary and discussions

We have derived the modified fluctuation relation for the heat given in (26) in general overdamped Langevin systems. It involves the extra factor $\Psi(Q)$ defined in (25) which reflects the correlation between the dissipated heat and the energy change of the system. We have investigated the mutual correlations in a two-dimensional linear diffusion system, which is exactly solvable by using the method presented in Appendix A. We have obtained the closed form expressions for the LDFs for the probability distributions in (55), (58), (63), (73), and (75). In particular, the result shows that the heat and the energy change are negatively correlated. It is manifested in $e_{pr}(q)$ that corresponds to the value of e minimizing $\pi_{\text{he}}(q, e)$ with fixed q , i.e., the most probable energy change to a given heat dissipation. It is nonzero for large values of q as shown in (76), and gives rise to a nonzero value of $\psi(q)$. Therefore, we conclude that the negative correlation is the origin for the distinct fluctuation property of the heat.

In this work, we only study the simplest linear diffusion system with the force matrix given in (40). A natural direction for future works is to consider a general force matrix having different diagonal elements, which can describe experimental systems such as a coupled RC circuit investigated in Ref. [46]. It will be interesting to study the correlations in the anisotropic system. It will be also interesting to study the correlations in nonlinear systems. We hope that our work triggers further theoretical and experimental studies.

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Appendix A. Joint distributions in linear diffusion systems

In this Appendix, we introduce a path integral formalism for the MGF $G_{\text{we}}(\lambda, \kappa)$ in a linear diffusion system where the force is given by the form in (36). It is an extension of the path integral formalism for $G_{\text{w}}(\lambda)$ developed in Ref. [33].

Suppose that the initial configuration $\mathbf{x}(t_i)$ follows the distribution given by

$$P_i(\mathbf{x}) = \sqrt{\det\left(\frac{\mathbf{S}}{2\pi}\right)} e^{-\frac{1}{2}\mathbf{x}^T \cdot \mathbf{S} \cdot \mathbf{x}} \quad (\text{A.1})$$

with a symmetric positive-definite matrix \mathbf{S} . The equilibrium Boltzmann distribution is obtained by taking $\mathbf{S} = \mathbf{F}_s$. In general, it can be taken arbitrarily depending on a physical condition. The MGF $G_w(\lambda)$ is given by [33]

$$G_w(\lambda) = \int [D\mathbf{x}(t)] \mathcal{T}[\mathbf{x}(t)|\mathbf{x}(t_i)] P_i(\mathbf{x}(t_i)) e^{-\lambda \mathcal{W}[\mathbf{x}(t)]} , \quad (\text{A.2})$$

where $\mathcal{T}[\mathbf{x}(t)|\mathbf{x}(t_i)]$ is the conditional probability for a path $\mathbf{x}(t)$ to a given initial configuration $\mathbf{x}(t_i)$ and the work is given in (37). The Onsager-Machlup formalism [40, 48] allows one to write the conditional probability as

$$\mathcal{T}[\mathbf{x}(t)|\mathbf{x}(t_i)] \propto e^{-\frac{1}{4} \int_{t_i}^{t_f} dt |\dot{\mathbf{x}}(t) - \mathbf{f}(\mathbf{x}(t))|^2 - \frac{1}{2} \nabla_{\mathbf{x}} \cdot \mathbf{f}(t)} \quad (\text{A.3})$$

with the Stratonovich integral. Note that the exponents in (37), (A.1), and (A.3) are quadratic in \mathbf{x} . Hence, $G_w(\lambda)$ in (A.2) can be evaluated by the Gaussian integration in principle.

The Gaussian integration can be evaluated efficiently. First, discretize the time and introduce $\{\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_M\}$ with $\mathbf{x}_k = \mathbf{x}(t_k = t_i + k(t_f - t_i)/M)$ representing the configuration at k -th time slice. Then, the MFT in (A.2) is written in the form of

$$G_w(\lambda) \propto \int \left[d\mathbf{x}_M \prod_{k=0}^{M-1} d\mathbf{x}_k e^{-K_k(\mathbf{x}_{k+1}, \mathbf{x}_k)} \right] e^{-\mathbf{x}_0^T \cdot \mathbf{S} \cdot \mathbf{x}_0} ,$$

where $K_k(\mathbf{x}_{k+1}, \mathbf{x}_k)$ is quadratic in both \mathbf{x}_x and \mathbf{x}_{k+1} that is determined from the expressions for \mathcal{T} and \mathcal{W} [33]. The kernel for \mathbf{x}_0 is \mathbf{S} . Since \mathbf{x}_0 is coupled to \mathbf{x}_1 through K_0 , one obtains an effective kernel for \mathbf{x}_1 after integrating over \mathbf{x}_0 . It is done successively to obtain a recursion relation for the kernel, denoted by $\tilde{\mathbf{A}}(t_k)$, for $\mathbf{x}(t_k)$. In the $M \rightarrow \infty$ limit, the recursion relation can be casted into the differential equation

$$\frac{d\tilde{\mathbf{A}}}{dt} = -2\tilde{\mathbf{A}}^2 + \tilde{\mathbf{A}}\tilde{\mathbf{F}} + \tilde{\mathbf{F}}^T\tilde{\mathbf{A}} + \Lambda , \quad (\text{A.4})$$

where $\tilde{\mathbf{F}} = \mathbf{F} - \lambda(\mathbf{F} - \mathbf{F}^T)$ and $\Lambda = (\mathbf{F}^T\mathbf{F} - \tilde{\mathbf{F}}^T\tilde{\mathbf{F}})/2$. The initial condition is given by

$$\tilde{\mathbf{A}}(t_i) = \mathbf{S} . \quad (\text{A.5})$$

Collecting all the factors coming from the all integrations, one obtains that

$$G_w(\lambda) = \sqrt{\frac{\det(\mathbf{S})}{\det(\tilde{\mathbf{A}}(t_f))}} e^{-\int_{t_i}^{t_f} dt \text{Tr}(\tilde{\mathbf{A}}(t) - \tilde{\mathbf{F}})} . \quad (\text{A.6})$$

The factor $\det(\mathbf{S})$ originates from the normalization factor of P_i in (A.1) and the factor $\det(\tilde{\mathbf{A}}(t_f))$ from the final Gaussian integration over $\mathbf{x}(t_f)$. The exponential factor accounts for the contribution from the intermediate time steps [33].

The formal expression for $G_{\text{we}}(\lambda, \eta)$ is given by

$$G_{\text{we}}(\lambda, \kappa) = \int [D\mathbf{x}(t)] \mathcal{T}[\mathbf{x}(t)|\mathbf{x}(t_i)] P_i(\mathbf{x}(t_i)) \times e^{-\lambda \mathcal{W}[\mathbf{x}(t)] - \kappa \Delta \mathcal{E}[\mathbf{x}(t)]} \quad (\text{A.7})$$

Note that $\Delta \mathcal{E}[\mathbf{x}]$ is also quadratic in \mathbf{x} . Hence, G_{we} can be evaluated using the same method. Comparing the integrands in (A.2) and (A.7), one finds that they differ by the boundary term $-\kappa \Delta \mathcal{E}[\mathbf{x}(t)] = -\frac{\kappa}{2} \mathbf{x}(t_f)^T \cdot \mathbf{F}_s \cdot \mathbf{x}(t_f) + \frac{\kappa}{2} \mathbf{x}(t_i)^T \cdot \mathbf{F}_s \cdot \mathbf{x}(t_i)$ in the exponent. Consequently, $G_{\text{we}}(\lambda, \kappa)$ is simply obtained by replacing \mathbf{S} in (A.5) with $(\mathbf{S} - \kappa \mathbf{F}_s)$ and $\tilde{\mathbf{A}}(t_f)$ in (A.6) with $(\tilde{\mathbf{A}}(t_f) + \kappa \mathbf{F}_s)$. Therefore, we obtain

$$G_{\text{we}}(\lambda, \kappa) = \sqrt{\frac{\det(\mathbf{S})}{\det(\tilde{\mathbf{A}}(t_f) + \kappa \mathbf{F}_s)}} e^{-\int_{t_i}^{t_f} dt \text{Tr}(\tilde{\mathbf{A}}(t) - \tilde{\mathbf{F}})} \quad (\text{A.8})$$

where $\tilde{\mathbf{A}}(t)$ is the solution of (A.4) with the shifted initial condition

$$\tilde{\mathbf{A}}(t_i) = \mathbf{S} - \kappa \mathbf{F}_s \quad (\text{A.9})$$

The initial state of the system at time $t = t_i$ is characterized by \mathbf{S} . If one takes the equilibrium Boltzmann distribution as the initial state, it should be taken as

$$\mathbf{S} = \mathbf{F}_s \quad (\text{A.10})$$

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